III.A.30 Fundamental Studies of the Durability of Materials for Interconnects in Solid Oxide Fuel Cells

Objectives

- Develop mechanism-based evaluation procedures for the stability of SOFC interconnect materials and use these procedures to study and modify a group of alloys, which have already been identified as candidate interconnect materials, i.e., ferritic stainless steels.
- Study fundamental aspects underlying the thermomechanical behavior of interconnect materials and develop accelerated testing protocols. (CMU Subcontract)
- Investigate the potential for the use of "new" metals as interconnect materials.
- Develop a durable, conductive ceramic/metal (cermet) material, suitable for long-term use as a contacting material in the cathode chamber of a SOFC. (WVU Subcontract)

Accomplishments

- Determined that even very small concentrations of Al or Si in ferritic alloys (on the order of tenths of a percent) result in the formation of internal films with high electrical resistivity.
- Discovered that exposure under some fuel cell operating conditions (e.g., water vapor) accelerates sigma phase formation in some ferritic stainless steels. Alloy purity is also important for retarding sigma phase formation.
- Discovered that it is possible to modify a ferritic stainless steel to form an overlayer of TiO_2 which suppresses the evaporation from the underlying chromia scale.
- Determined that the growth rate of chromia on ferritic alloys can be greatly suppressed by surface doping with CeO_2.
- Found that the growth rate of NiO can be slowed significantly by surface doping with SrO or CeO_2.
- Found that, unlike ferrous alloys, the oxidation of Ni is not altered significantly under dual atmosphere conditions.
- Showed that Ni interconnects containing Ag conduction paths are feasible.
- Developed an image analysis technique for analyzing indentation-induced chromia scale flaking failures for interconnects exposed in wet air [simulated cathode gas (SCG)].
- Exposed 26 Cr Ferritic alloy specimens to a range of short-term SCG exposures at 900°C, performed indentation tests, and tracked the evolution of flaking-type spallation failures with exposure.
- Completed three M.S. theses and six Senior Projects.

Gerald H. Meier (Primary Contact), Frederick S. Pettit
Department of Materials Science and Engineering
848 Benedum Hall
University of Pittsburgh
Pittsburgh, PA 15261
Phone: (412) 624-9720; Fax: (412) 624-8069
E-mail: ghmeier@engr.pitt.edu, pettit@engr.pitt.edu

DOE Project Manager:
Ayyakkannu Manivannan
Phone: (304) 285-2078; Fax: (304) 285-4403
E-mail: Ayyakkannu.Manivannan@netl.doe.gov

Subcontractors:

1. Jack L. Beuth, Carnegie Mellon University (CMU)
Phone: (412) 268-3873; Fax: (412) 268-3348
E-mail: beuth@andrew.cmu.edu

2. James R. Rakowski, ATI Allegheny Ludlum
Phone: (724) 226-6383; Fax: (724) 226-5067
E-mail: JRakowski@AlleghenyLudlum.com

3. Bruce Kang, West Virginia University (WVU)
Phone: (304) 293-3111 x2316; Fax: (304) 293-6689
E-mail: bruce.kang@mail.wvu.edu

Introduction

Solid oxide fuel cells provide a potential way to generate electricity with high efficiency and low pollution. The operating principles of fuel cells have been known for over 100 years, and low-temperature fuel cells provided the electric power on all the Gemini and Apollo spacecraft. However, fuel cells have not achieved widespread commercial use for a number of economic and technical reasons.

One of the most important technical challenges for solid oxide fuel cells, which operate in the temperature range 700°-900°C, is the design of interconnects (current collectors). These components, in addition to electrically connecting individual cells in a stack, must separate the anode compartment of one cell from the cathode compartment of the adjacent cell. This means that one side of an interconnect is exposed to the fuel, typically hydrogen or hydrocarbons in which the oxygen partial pressure is low, and the other side is exposed to the oxidant, which is typically air with some amount of water vapor. Metallic alloys have many attractive features as potential interconnect materials.

Oxidation resistant alloys are designed to form one of three protective oxides: alumina, silica, or chromia. Of these, the electrical resistivities of alumina and silica are much too high for interconnect applications. For metallic interconnects, interconnect system resistance can be greatly increased by oxide layer thickening and spallation. For chromia formers, evaporation of the chromia scale can severely degrade cathode performance. Thus, chromia scale growth, scale spallation and scale evaporation are the three principal “failure mechanisms” for interconnects forming chromia scales on their surfaces. Because the mechanisms are coupled, alloy changes to address one failure mechanism can affect one or more of the other failure mechanisms, making alloy design a complex task.

Approach

The project consists of four major tasks aligned with its four objectives.

Task 1. Mechanism-based Evaluation Procedures

A variety of chromia-forming interconnect alloys are being subjected to thermal cycling in air, in simulated anode gas (Ar-H_2-H_2O) and with simultaneous exposure to air on one side and simulated anode gas on the other. Combined exposures have been shown at Pacific Northwest National Laboratory to often yield different behavior than exposures with the same gas on both sides of the specimen. Exposure temperatures range from 700°C to 900°C. Oxidation kinetics is being tracked by mass change measurements, and corresponding changes in oxide scale resistances are being measured. Exposed specimens are being examined in cross-section by scanning electron microscopy (SEM) to document changes in structure with exposure.

Methods are being studied to slow the growth of chromia scales on Cr and Ferritic alloys with exposure, to decrease the contribution of the scale to interconnect resistance. The effect of alloying additions (e.g., Mn, Ti) to ferritic steels to reduce harmful CrO_3 and $CrO_2(OH)_2$ evaporation by forming a sealing outer layer over the chromia scale is being evaluated. The ability of chromite coatings to reduce evaporation from chromia-forming interconnect alloys is also being investigated.

Task 2. Fundamental Aspects of Thermomechanical Behavior (CMU)

Understanding the resistance of growing chromia scales to spallation requires a fundamental understanding of the mechanics of chromia adhesion. From a fracture mechanics standpoint, the adherence of protective oxide scales to alloy substrates is governed by 1) the stored elastic energy in the scale, which drives delamination, and 2) the fracture toughness of the alloy/oxide interface, which quantifies the resistance to fracture.

The stored elastic energy in the scale is increased by increases in the scale thickness (which can be measured by cross-section SEM) and increases in the residual stress in the scale. In this task, x-ray diffraction (XRD) is being used to measure stresses in chromia films formed on pure chromium and chromia-forming alloys after the exposures described for Task 1.

An indentation test is also being used to quantify the fracture toughness of chromia/alloy interfaces for the same exposures. In the test, the chromia scale is penetrated by the indenter, and the plastic deformation of the underlying substrate induces compressive radial strains in the substrate. These strains are transferred to the scale, and the associated scale stress drives scale spallation. Scales can spall as intact coatings, with an interface crack propagating radially outward, or spallation can occur as the debonding of small flakes, with the density of flaking decreasing with distance from the indent. The interfacial toughness can be estimated from the results of a mechanics analysis of the indentation problem and a measurement of the extent of the delamination failures.

Task 3. Alternative Material Choices

Metallic materials other than chromia-formers are being considered for use as low-temperature SOFC interconnects. Experiments similar to those described for Task 1 are being performed on pure Ni. Its only oxide, NiO, has no vapor species with high partial pressures and has a higher electrical conductivity than chromia. Also, NiO should not even form in the anode gas. The doping of the NiO scale with SrO or CeO_2 is being investigated as a way to slow the growth rate. Finally, the use of Ag conducting paths through Ni interconnects is being studied.

Task 4. Development of Durable Contacting Material (WVU)

At present, candidate cermets have been developed by ball-milling of various oxide powders with silver or silver-oxide powders, followed by dry-pressing and sintering in a high-temperature furnace. The cermets are evaluated by SEM to determine the compatibility of silver with the candidate oxide materials, as well as the dispersion of silver throughout the cermet. The cermets are also tested for hardness/ductility using Vickers hardness testing. At this time, conductivity is evaluated using a simple multimeter test to evaluate the resistance of the cermet. A thermomechanical analyzer is also used to evaluate the coefficient of thermal expansion of the materials to verify compatibility with other SOFC components. Lastly, cermets are placed in a high-temperature furnace to be exposed to the SOFC operating temperature (~800˚C), while a high-volume air flow is introduced to simulate the cathode environment of the SOFC.

All measurements–conductivity, hardness, and mass–are taken before and after exposure to the simulated cathode environment in order to make a determination of the effects on the cermet material.

Results

Task 1. Mechanism-based Evaluation Procedures

In attempts to reduce the growth rate of chromia and, therefore, the electrical resistance, E-Brite samples have been doped with CeO_2 using pulsed laser deposition. Oxidation experiments for 100 hours at 800°C in air show that the doping drastically reduced the thickness of the chromia scale.

Sigma phase was observed to form at 700°C in the alloys with higher chromium concentrations, e.g., 26 Cr Ferritic and E-BRITE. Sigma phase is promoted in these alloys by the presence of Mo. (Additions of W would have a similar effect.) It was also found that impurity elements, such as Si, accelerated the formation of the sigma phase, e.g., 26 Cr Ferritic developed this phase more rapidly than did E-BRITE. A previously unknown result was that sigma phase formation was dramatically accelerated in atmospheres containing water vapor. Sigma phase must be avoided since it is very brittle and tends to crack.

It was found that even small amounts of Al or Si (less than 0.5 wt %) in ferritic steels result in the formation of continuous alumina or silica films, which greatly increases the area specific resistance. Therefore, future alloy development should hold these elements to the minimum values possible.

A major problem with chromia-forming alloys is oxide volatility as CrO_3, particularly in the cathode gas, since the CrO_3 partial pressure increases with oxygen partial pressure. The volatile species are reduced at electrochemically active sites on the cathode during SOFC operation, which inhibits the required oxygen reduction. Analysis of the Cr vapor species indicates that water contents above about 0.1% in air result in partial pressures of $CrO_2(OH)_2$ which exceed the partial pressure of CrO_3 and result in cathode poisoning. There are three potential solutions to this problem:

1. Develop cathode materials that are not affected by Cr contamination.
2. Suppress the evaporation of Cr species from ferritic alloys.
3. Develop Cr-free materials with suitable interconnect properties.

The latter two approaches are being pursued in this research. Approach 3 is described in Task 3 below.

An ideal approach to suppressing Cr volatility would be to develop an alloy which forms a Cr-free oxide overlayer. Experiments on Ni-base superalloys indicated that Ti additions might provide such a layer. Four heats of novel Fe-Cr-Ti alloys with Ti contents varying between 1 and 4 wt% and one Ti-free control heat were produced in a vacuum induction melting furnace in the form of fifty-pound ingots at ATI Allegheny Ludlum. Isothermal and cyclic oxidation experiments indicate that indeed these alloys can form a continuous TiO_2 overlayer, and this layer is very effective in reducing chromia evaporation. A patent disclosure has been filed, and this alloy system is being vigorously pursued.

Task 2. Fundamental Aspects of Thermomechanical Behavior (CMU)

Previous reports have described the indentation fracture testing of ferritic stainless steel alloys exposed to simulated anode gas (SAG) $Ar/H_2/H_2O$ environments. Indented chromia scales formed in SAG debond as an intact coating, and the radial extent of the debonding observed in short-term exposures has been used to estimate the long-term exposure time when spallation can occur. Previous reports also presented indentation results for ferritic stainless steels exposed in air with 0.1 atm H_2O, representing a moist SCG environment. When indented, those specimens exhibited a flaking type of debonding with a decreasing density of flaking with radial distance from the indent. Results for both types of tests are summarized in the paper by Dhanaraj et al. [1].

In this past year, an image analysis technique has been developed to analyze the failures seen in SCG-exposed interconnects. In these specimens, bonded areas are black or dark grey, which is the shade of the chromia scale. Areas of spallation appear white or very light grey due to the exposed metal substrate. The imaging technique involves quantifying the distribution of white/grey/black pixels in a single image in regions far from the indentation. The distributions of greys in 5-7 rings around the indentation are also determined. The percentage of debonding in a ring is determined by subtracting the distributions of grey from that ring from the far-field image distribution. The result from the analysis of multiple rings is a plot of the percentage of debonding scale vs. radial distance from the debond. Results from images taken after different exposures allow the tracking of debonding vs. radius as a function of exposure.

Figure 1 gives an example of results from this type of analysis. In the figure, images from indentation of a 26 Cr Ferritic alloy exposed in SCG from 10 to 200 hours have been analyzed. Images at 10 and 200 hours are included in the figure, as is a plot of the percentage of debonding vs. R/a for different exposures. R is the

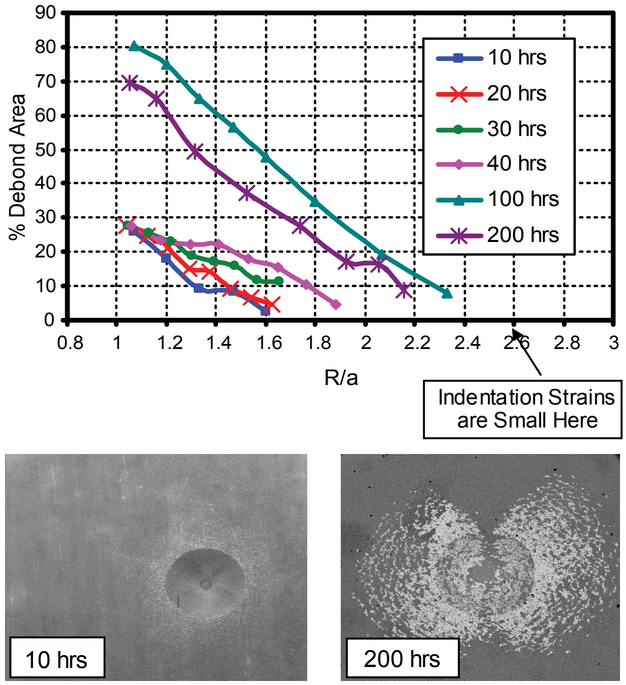

FIGURE 1. Percentage of Debonding vs. Radial Distance for a 26 Cr Ferritic Alloy Exposed in Wet Air (Simulated Cathode Gas) at 900°C for 10 – 200 Hours

radial distance from the indentation and a is the radius of the indentation. The images taken in these tests show a fairly consistent decrease in debonding density with radius and an increase in debonding density with exposure. Plots of debond percentage vs. R/a from the image analyses are consistent with these qualitative observations. As exposures are increased, the curves of percentage debonding rise, but the increases in debonding stop at 100-200 hours of exposure. At this point, some amount of debonding is observed even at radial distances where the strains due to indentation are almost zero.

The conclusion from these results is that after 100-200 hours of exposure in SCG at 900°C, spontaneous spallation (spallation that can occur without the use of indentation) has begun to occur. At this point, spontaneous spalls (and perhaps some scale evaporation) act to keep the average thickness of the chromia scale more or less constant, so that plots of debond percentage vs. R/a reach a steady-state. This is consistent with weight gain measurements performed as part of Task 1 of this project. Weight gains in these specimens stop after 100 hrs of exposure, and specimen weight remains constant from that point on.

Task 3. Alternative Material Choices

Experiments are being carried out on pure Ni as a possible alternative interconnect material since the oxygen partial pressure in the anode gas is too low to oxidize Ni. The primary challenge in making Ni perform satisfactorily as an interconnect is to reduce the electrical resistance of the thermally grown oxide that forms on the cathode side during fuel cell operation.

Efforts to decrease the electrical resistance of the interconnect oxide are twofold. First, we are trying to reduce the scale thickness by the use of surface dopants. Pulsed laser deposition is used to deposit thin films of SrO and CeO_2 onto the surface of nickel. Our tests have shown that CeO_2 decreases the thickness of NiO by a factor of 4 (Figure 2) and SrO doping decreases it by a factor of 2. Area specific resistance is proportional to scale thickness, and the resistance decreases accordingly. These dopants can be deposited by inexpensive techniques once the optimum dopants are identified.

Finally, the resistance introduced by the thermally grown oxide is being by-passed by the use of high-conductivity pathways. Silver is not considered as a possible interconnect material due to the high permeability of hydrogen and oxygen in silver, which causes water nucleation and mechanical instability. However, silver may be able to provide a high-conductivity pathway through another material. Systems in which silver wires are passed through nickel and silver powder is melted into holes drilled in nickel are being examined. Figure 3 shows the cross-section of a Ni specimen where Ag has been melted in a hole drilled in the Ni. After exposure there is some porosity in the silver, and it appears the grain boundaries are delineated with pores far into the silver. Importantly, despite the porosity, the specimen had resistance values typical of a metal when measured at room temperature following exposure. In this configuration, the Ni provides the physical integrity of the interconnect and the silver only provides the conduction path through the scale.

Task 4. Development of Durable Contacting Material (WVU)

Samples have been fabricated using various compositions of silver and differing oxides such as lanthanum strontium manganese oxide (LSM) and copper oxide. The samples were fabricated by dry

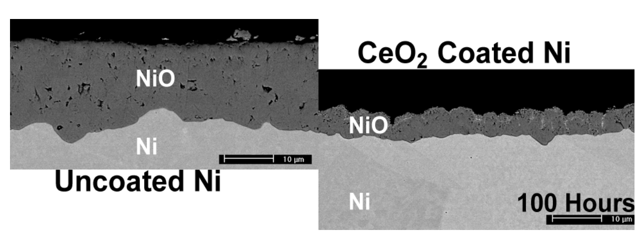

FIGURE 2. Effect of CeO_2 Deposited by Pulsed Laser Deposition on the Growth Rate of NiO at 800°C in Dry Air

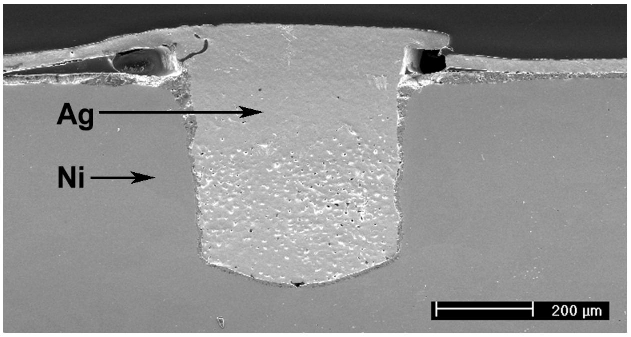

FIGURE 3. Silver Via, 800°C, 100 hours, exposed under dual atmospheric conditions. The upper surface was exposed to dry air while the lower surface was exposed to simulated anode gas of Ar-10%H_2O-4%H_2.

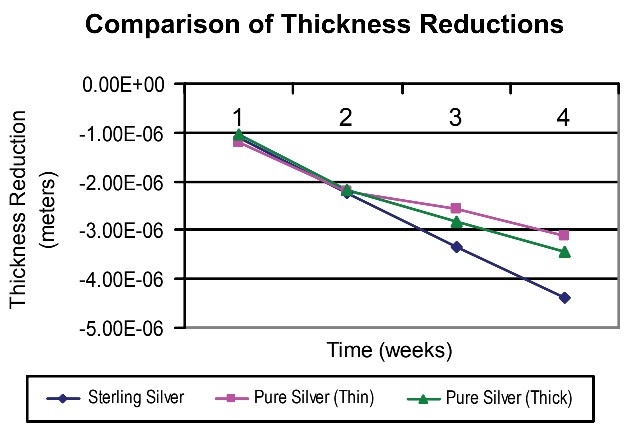

FIGURE 4. Comparison of Thickness Reductions for Various Silver Samples

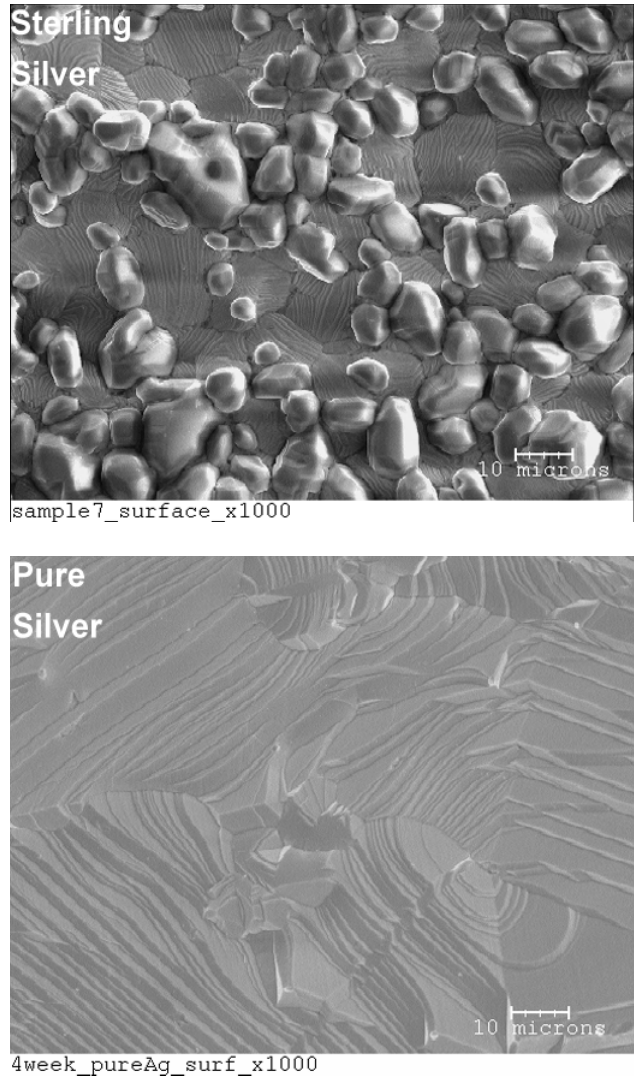

FIGURE 5. SEM Micrograph Comparison of Sterling and Pure Silver Samples after 3-Week High-Temperature Exposure

pressing followed by sintering at high temperature for various periods of time. It was determined that this method did not result in samples that were robust enough for use in the high-temperature evaporation experiments. In order to fabricate samples that were durable enough for testing, it was decided that the method of fabrication be modified. Instead of the ball-milling/pressing/sintering method previously used, it was decided that the oxidation of specific alloys would be a simpler method to produce reliable samples.

Sterling silver has been identified as a candidate for use as a contacting material due to its favorable composition and low cost. Upon oxidation, the copper in the sample becomes copper oxide, which is meant to act as a barrier against evaporation of the silver in the sample, extending the usable life of the cermet. Sterling silver is currently being tested in high-temperature exposure alongside pure silver to gain an understanding of the performance of copper oxide in protecting against silver evaporation. Early results are shown in Figure 4.

It appears that all samples exhibit similar evaporation behavior very early on; however, after several weeks, it appears that the rate of loss for the pure silver samples is lower than that for the sterling silver sample. Samples are also regularly examined for surface changes due to high-temperature exposure. Examples of SEM micrographs for exposed samples are shown in Figure 5.

The sample surfaces exhibit clearly different behavior which may affect the evaporation rates of the samples. Future work will continue to examine the evaporation of sterling silver over long-term high-temperature conditions to evaluate the effect of copper oxide on silver evaporation rate as well as examine surface microstructure changes of the sample.

Another method of fabrication utilizing ball-milling/pressing/hot-pressing is also being developed to fabricate samples composed of Ag/LSM and Ag/cerium. The hot-pressing technique is meant to aid in better dispersion of oxide in the sample as well as make the sample more suitable in terms of robustness for the long-term high-temperature testing.

Conclusions and Future Directions

The project is currently operating under a no-cost extension with an end-date of June 30, 2006. The remaining activities will be completion of a study of methods to seal cracks in $LaCrO_3$ coatings on ferritic alloys and the preparation of the final report.

Special Recognitions & Awards/Patents Issued

1. Provisional patent application: "Iron-chromium-titanium Alloys that Restrict Evaporation of Chromium-containing Vapor Species at Elevated Temperatures"

FY 2006 Publications/Presentations

1. J. E. Hammer, S. J. Laney, R. W. Jackson, F. S. Pettit, and G. H. Meier, "Oxidation Problems Associated with Interconnects in Solid Oxide Fuel Cells", ASM International/TMS, "Materials Solutions", Pittsburgh, PA, September 2005.

2. Q. Ma and J. L. Beuth, Carnegie Mellon University; F. S. Pettit, G. H. Meier, and M. J. Stiger, University of Pittsburgh, "Use of Indentation Fracture Tests to Investigate Toughness Loss Mechanisms in Thermal Barrier Coating Systems", ASM International/TMS, "Materials Solutions", Pittsburgh, PA, September 2005.

3. J. L. Beuth and N. Dhanaraj, Carnegie Mellon University; J. E. Hammer, S. J. Laney, F. S. Pettit, and G. H. Meier, University of Pittsburgh, "Interfacial Fracture Testing to Evaluate the Durability of SOFC Interconnect Alloys", ASM International/TMS, "Materials Solutions", Pittsburgh, PA, September 2005.

4. Professors F. S. Pettit and G. H. Meier presented a two-day course (September 22-23, 2005) on "Science and Technology of Advanced Metallic Systems for Applications in Intermediate Temperature Solid Oxide Fuel Cells (SOFCs)" at the National Energy Technology Laboratory (NETL). The course was attended by approximately thirty scientists and engineers at the NETL site in Morgantown, WV and webcast to universities, national laboratories, and industrial laboratories around the U. S.

5. S. J. Laney, R. W. Jackson, F. S. Pettit, and G. H. Meier, University of Pittsburgh; J. R. Rakowski, ATI-Allegheny Ludlum, "The Effects of Dual Environments and Chromia Evaporation on Metallic Interconnect Behavior", TMS Annual Meeting, San Antonio, TX, March 2006.

6. Q. Ma, J. L. Beuth, F. S. Pettit, G. H. Meier, and M. J. Stiger, "Use of Indentation Fracture Tests to Investigate Toughness Loss Mechanisms in Thermal Barrier Coating Systems", <u>Coatings 2005</u> (Nitin Padture, Lorraine Francis, Janet Hampikian and Narendra Dahotre, eds.) Proc. Materials Science and Technology 2005, Pittsburgh, September 2005, pp. 3-6.

7. N. Dhanaraj, J. L. Beuth, G. H. Meier, F. S. Pettit, J. Hammer, and S. J. Laney, "Interfacial Fracture Testing to Evaluate the Durability of SOFC Interconnect Alloys", <u>Materials for the Hydrogen Economy</u> (J. J. Petrovic, I. E. Anderson, T. M. Adams, G. Sandrock, C. F. Legzdins, J. W. Stevenson, and Z. G. Yang, eds.), Proc. Materials Science and Technology 2005, Pittsburgh, September 2005, pp. 165-175.

References

1. N. Dhanaraj, J. L. Beuth, G. H. Meier, F. S. Pettit, J. Hammer, and S. J. Laney, "Interfacial Fracture Testing to Evaluate the Durability of SOFC Interconnect Alloys", Materials for the Hydrogen Economy (J. J. Petrovic, I. E. Anderson, T. M. Adams, G. Sandrock, C. F. Legzdins, J. W. Stevenson, and Z. G. Yang, eds.), Proc. Materials Science and Technology 2005, Pittsburgh, September 2005, pp. 165-175.